Rediscovery of the Elements

Fluorine and Henri Moissan

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Elemental fluorine is so reactive that even asbestos burns in it![1] The search for fluorine poisoned many researchers and probably shortened the life of Scheele, who originally prepared HF in 1771, and Moissan, who first isolated elemental fluorine in 1886.[2] (Note 1) For no other element has there been so long a period of time between the characterization of its compounds and the preparation of it in its elemental state.

Faculté de Pharmacie, rue de l'Observatoire. In 1667 the Royal Observatory of Paris was opened with great fanfare on the southern outskirts of Paris (Figure 1). The first director was Jean-Dominique Cassini (1625–1712), for whom the famous division in Saturn's rings was named. Accomplished scientists were soon attracted to the observatory; a plaque today outside the observatory informs us that Ole Christensen Römer (1644–1710), visiting from Denmark, in 1676 first measured the speed of light from observations of Jupiter's moons.[3] The metric units of mass (gram) and length (meter) were defined following measurements and researches made at the observatory during the latter part of the 18th century.[3] In 1851 Jean Bernard Léon Foucault (1819–1868) proclaimed to all scientists, "Vous êtes invités à venir voir tourner la terre . . ." ["You are invited to see the earth turn"] as he set up his famous pendulum in the observatory and presented the first public demonstration of the rotation of the earth.[3]

In 1811 the rue de l'Observatoire was laid northward toward the luxurious Luxembourg Gardens (Jardin du Luxembourg, Figure 2). Today, as one strolls northward from the Royal

Figure 1. (Above) The Royal Observatory of Paris, at the southern terminus of rue de l'Observatoire. (Bottom left) The view of the observatory according to the Turgot Map[13] of 1739. (Bottom right) Northward from the observatory as far as the Seine, 15-centimeter bronze disks can be spotted with the name of [Dominique François Jean] Arago (1786-1853), who helped lay out the Méridien de Paris, used universally until 1884 for 0° longitude. Humboldt in his Mexican travels[14] used this as his "prime meridian," actually 2° 20.20 east of the current Greenwich, England, meridian.

Observatory along the beautiful chestnut-lined walkways of Luxembourg Gardens, one can follow the trail of 15-cm bronze disks (see Figure 1) identifying the Paris meridian, radiating northward as far as the Seine. This is the line that Humboldt used as the zero meridian in his longitude calculations in Mexico.[4]

Adjoining the Luxembourg Gardens on the rue de l'Observatoire is the present Faculté de Pharmacie (Figure 3), which moved from its previous location on rue de l'Arbalète in 1882 (Note 2). Among the faculty that made the

Figure 2. At opposite ends of rue de l'Observatoire lies the Paris Observatory (A; N 48° 50.18, E 02° 20.20) and the Moissan Museum (B), located in the Faculté de Pharmacy, 4, rue de l'Observatoire (N 48° 50.58, E 02° 20.18). The fluorine research was performed in Debray's laboratory on rue Michelet, 50 meters south (B). Other notable sites in the general area include (C) the Sorbonne, (D) Curie Institute and Museum, and (E) Notre Dame Cathedral.

move in 1882 was the young chemist Ferdinand-Frédéric-Henri Moissan (1852-1907), who had joined the institute in 1879. Through his work on the electric arc furnace and the preparation of elemental fluorine, Henri Moissan became famous at the Faculté de Pharmacie, winning the Nobel Prize in 1906.[2]

Today the Faculté de Pharmacie houses the Musée Henri Moissan (Moissan Museum), a large salon maintained by Professeur Jérôme Dugué and filled with "les souvenirs d'Henri Moissan"—exhibits and mementos, including diplomas of the Nobel Prize and other decorations, documents, photographs, and books. The museum is open only by appointment; we had to make a reservation months in advance.

During the prescribed day, our patience was well rewarded with a guided tour by a visiting

Figure 3. Faculté de Pharmacie. In the courtyard (lower right, not shown) is a statue of Vauquelin, the discoverer of chromium and beryllium (see ref 4 for a photograph).

Figure 4. Le Professeur émérite Jacques Rivet holding a special metal tube constructed by Henri Moissan used to study elemental, gaseous fluorine. Capped with transparent, inert fluorite caps, the tube allowed Moissan to observe for the first time that the color of elemental fluorine is yellow.

expert of the life of Henri Moissan—le Professeur émérite Jacques Rivet. For an afternoon we were captivated as Professeur Rivet, elegant and poetic, gave a three-hour presentation on the life and accomplishments of Henri Moissan, moving from showcase to showcase in the expansive hall (Figure 4).

Moissan (Professeur Rivat related in his narrative) was born in Paris but moved to Meaux (40 km east) when he was 12. Later he was apprenticed at the Bandry apothecary in Paris (at the corner of rue Pernelle and rue Saint Denis, 1.93 kilometers north, across the Seine). After studying with Edmond Fremy (1814–1894; discovered "Fremy's salt," $NO(SO_3Na)_2$, in 1845) at the Muséum d'Histoire Naturelle, in 1879 he accepted a position at the École Supérieure de Pharmacie. In 1882, when the school moved to its present position, Moissan married Léonie Lugan, the daughter of a pharmacist in Meaux. This marriage was most fortunate, because her devotion and support allowed Moissan to pursue a most productive career, while his father-in-law gave financial support for his scientific endeavors.

Moissan originated his fluorine studies at a house on rue de Lancry (3.5 km northeast), but H.-J. Debray allowed him to use a more powerful battery in temporary barracks on the rue Michelet for his electrolysis studies (Note 3). This battery was designed after the one Robert Wilhelm Bunsen (1811–1899) had prepared, and with which he had recently prepared elemental rubidium (1863) and cesium (1882). The Debray laboratory, immediately around the corner from the Faculté de Pharmacie (Figure 2), was ramshackle, but ideal for Moissan's corrosive chemicals. Moissan first prepared elemen-

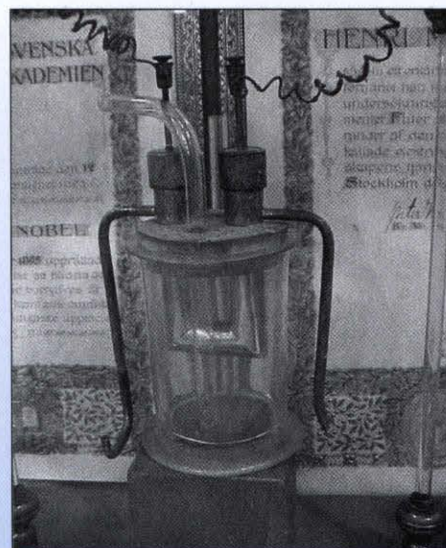

Figure 5. Exhibited in one of display cabinets in the Musée Moissan, the electrolysis apparatus used to produce elemental fluorine stands before Moissan's Nobel Prize certificate.

tal fluorine in 1886; the discovery was announced by Debray at the French Academy of Science meeting on 26 June 1886.[5] The key to Moissan's successful apparatus (Figure 5), as Professeur Rivat explained to us, was the combination of "French ingenuity" and four key ingredients:

(1) Finding a chemical system that was electrically conductive, that did not contain water, which would produce oxygen and not fluorine (KF/HF solution).

(2) Constructing an apparatus that was inert to elemental fluorine (fluorite, CaF_2).

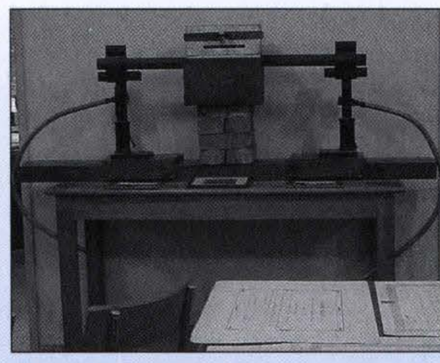

Figure 6. Moissan's electric arc furnace required huge amounts of energy and was run at the Edison Works in Paris.

(3) Utilizing inert electrodes at a cold temperature so the electrodes would not be attacked (Pt-Ir electrodes, in an apparatus contained with a condensed methyl chloride bath, -23° C).

(4) Using a chemical test which would prove the existence of elemental fluorine (spontaneous combustion with elemental silicon).

The shed on rue Michelet no longer existed, Rivat explained; it had been torn down because of months of savage abuse with corrosive chemicals. Even the windows were heavily fogged from reaction with hydrogen fluoride.

Moissan diversified his research to develop the "Moissan furnace" (Figure 6), an electric arc capable of temperatures as high as 3500° C. This furnace required prodigious quantities of electric power; Moissan first used the generating power at Gare de l'Est (railway station), but then settled on the Edison Works on Avenue Trudaine (4.3 km north of the Faculté de

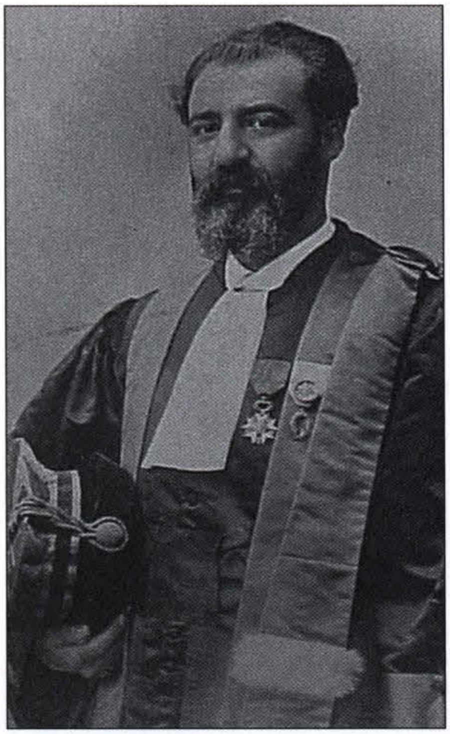

Figure 7. Moissan's portrait in the Salle des Actes, a grand hall with 91 other portraits of famed scientists associated in the Faculté de Pharmacie.

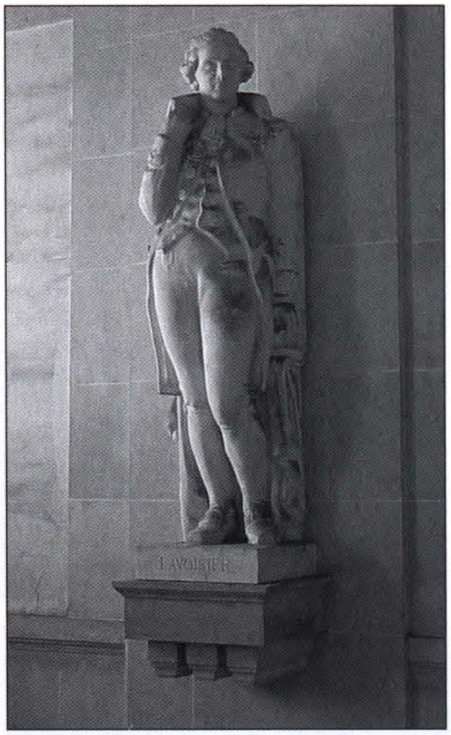

Figure 8. Lavoisier's statue in the Faculté de Pharmacie stands at the top of the second landing of the Faculté de Pharmacie (Note 4).

Pharmacie). In 1891 he first prepared carborundum, which has since been discovered in volcanic plugs and is named "moissanite." Moissan's goal was to prepare synthetic diamonds, and at the time it was believed he was successful. However, today it is doubtful that he was able to manufacture diamonds without high pressure; instead, he probably mistook carbide grit for his "crude diamond sand."

Moissan is credited with writing more than 300 works, his greatest being "Le Four Électrique" ("The electric-arc furnace," 1897), "Le Fluor et ses Composés" ("Fluorine and its compounds," 1900), and "Traité de Chimie Minerale" ("Treatise on inorganic chemistry," five volumes 1904–1906). He was an excellent lecturer and a meticulous and patient experimentalist.

Photographs and medals on the walls commemorate the presentation to Moissan of Commandeur de la Légion d'Honneur, his election as a member of the Académie de Médecine (1888), Académie des Sciences (1891), Conseil d'Hygiène de la Seine (1895), and the Comité Consultatif des Arts et Manufactures (1898). In 1887 Moissan was awarded the Prix Lacaze; he was a Davy medallist in 1896 and a Hofmann medallist in 1903. Moissan was honored by the Franklin Institute of Philadelphia and was awarded Fellowships of the Royal Society of London and The Chemical Society (London). He held honorary memberships in many other learned societies.

Moissan, in his later years, was in poor health, undoubtedly because of his exposure to poisonous chemicals. The year after he received his Nobel Prize, he died suddenly at the age of 54.

After our visit in the museum, we were then led out of the museum through an archway into the Salle des Actes, a huge ballroom where portraits of past professors of the university were displayed. Moissan's painting (Figure 7) was there, surrounded by the portraits of 91 other professors of the university during its four-century history. These portraits included Louis-Nicolas Vauquelin (1763–1829), first director of the École de Pharmacie (1803–1829), discoverer of chromium and beryllium; the family of Étienne François Geoffroy (1672–1731), who first articulated the "Table of Affinities" in 1718, a compilation of chemical trends, which allowed prediction of outcomes of other reactions; Guilliaume François Rouelle (1703–1770), demonstrator of chemistry 1742–1768 at the Jardin du Roi and the chemical instructor of Lavoisier during 1763–1764; and Antoine Baumé (1728–1804), who invented the hydrometer bearing his name in 1768.

The staircases of the Faculté de Pharmacie were adorned with beautiful stained-glass windows depicting the history of pharmacy and chemistry. One such window portrayed "Lavoiser dans son Laboratoire," and at the top of the staircase landing stood an 8-foot statue of Lavoisier (Figure 8). (Note 4).

Finally we returned to the Musée Moissan, where our guide proclaimed, "Je suis fini!" We settled down at a table where we were treated to the "haute cuisine" of the best wines and biscuits (Figure 9). After pleasant conversation about our families and friends in the U.S., we departed, tired but pleased with our full notebooks and camera disks.

Visiting Meaux. The next day, a one-hour train ride east took us to Meaux, east of Paris. This village celebrates its favorite son by a monument (Figure 10) dedicated to Moissan, next to the Lycée Moissan (high school). This monument was reached by a 10-minute walk from the train station, 350 meters northeast.

The Strange Story of Stinkspat. Fluorine is a relatively common element in the earth's crust (ranking 13th in abundance),[6] and yet because of its reactivity, fluorine has never been observed in its elemental state in nature.

Or has it? An unusual form of fluorite, which has been in extended contact with codeposited uranium minerals, can undergo devitrification to an incoherent form of a dark violet (virtually black) mineral called "Stinkspat." When crushed, it spawns a noxious, acrid odor. Anecdotal stories abound of ancient miners growing violently ill when digging up deposits of Stinkspat.[7]

In Wölsendorf, Germany, we visited a famous fluorite mine that has produced sizeable quantities of Stinkspat (Figure 11). Earlier

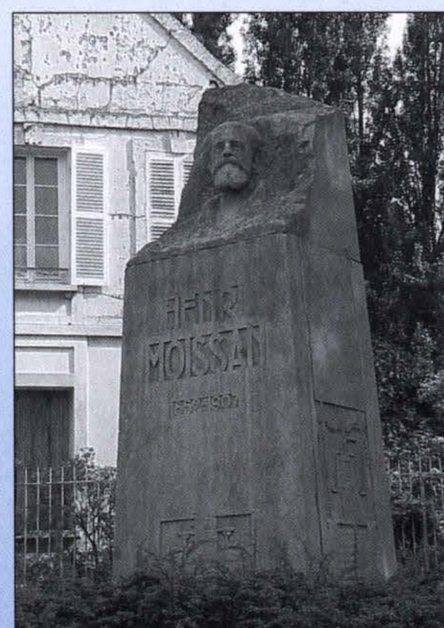

Figure 10. The Moissan monument in Meaux (Place Henri Moissan, N 48° 57.53, E 02° 52.68) is 40 kilometers east of the Faculté de Pharmacie. On the sides of the monument is a relief of the fluorine electrolysis apparatus (right) and his electric furnace (front).

Figure 9. The curator of the Moissan museum, Professeur Jérôme Dugué, Laboratoire de chimie physique et de chimie minérale (right), and Professeur émérite Jacques Rivet pour wine and prepare hors d'oeuvres in the style of typical warm French hospitality after Rivet's presentation to the authors.

Figure 11. Wölsendorf, Germany, is the site of "Stinkspat," a radioactive form of fluorine that produces inclusions of fluorine (N 49° 24.59, E 12° 11.24, 44 km north of Regensburg, Germany, and 35 km west of the Czech Republic).

research has reported that when Stinkspat is crushed, the released fluorine apparently reacts with water vapor to produce HF, then ozone, and finally hydrogen peroxide.[8,9] "Antozonite" was proposed as a name for this mineral variety of fluorite by Christian Friedrich Schönbein (1799–1868), the discoverer of ozone[10] in 1839; he also discovered guncotton[10] in 1845. Wöhler had also previously noticed the odor from crushed Stinkspat; and Moissan, familiar with the odor of F_2, verified its identity from the pulverized mineral.[8] Recent mass spectral studies[11] have shown that samples of Stinkspat contain quantities of carbon tetrafluoride and sulfur hexafluoride, the amount of which correlates with the amount of radioactivity present, but this experimental procedure is not able to confirm the evolution of F_2 or other corrosive gases.

Wishing to revisit the 19th-century experiment,[8] we crushed small (1 gram) quantities of Wölsendorf Stinkspat (Figure 12) in a mortar. There was indeed a foul odor, lasting only 2–5 seconds. We ground samples with "Schönbein paper" (prepared with potassium iodide and starch[10]) and verified by the developing blue color the presence of a powerful oxidizer (the blue color could subsequently be dissipated by the addition of thiosulfate solution). A "windowless" EDX (energy dispersive X-ray) analysis of the sample (which can detect elements with atomic numbers as low as 5) showed only Ca and F (and traces of Si, Mg, and Al; no O was detected). Apparently the oxidant does indeed arise from elemental fluorine! Our "Living Periodic Table"[12] is now complete—it now includes a specimen of Stinkspat, which allows us to claim a sample of fluorine "in the native state."

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Notes.

1. Even research with fluorine salts was dangerous; gaseous hydrogen fluoride itself is extremely poisonous. Sir Humphry Davy (1778–1829), successful in the electrolysis and reduction of reactive metal salts, was sickened, but recovered. Others who were poisoned by experiments with hydrogen fluoride include Joseph Louis Gay-Lussac (1778–1850) and Louis Jacques Thenard (1777–1857) of France, and George and Thomas Knox of Ireland. Among those who perished in the attempt to prepare elemental fluorine were Jérôme Nicklès (1820–1869) of Nancy, France, and Paulin Louyet (1818–1850) of Brussels, Belgium. George Gore (1826–1908) of Birmingham, England, experienced a violent explosion in 1869 while working with the electrolysis of fluoride salts.[15]

Figure 12 Stinkspat specimen from Wölsendorf, Germany. When ground in the presence of starch/KI paper, a blue color develops, showing the presence of a strong oxidizer (F_2 inclusions).

2. Nicolas-Louis Vauquelin (1763–1829) had been the director of the Pharmacie Institute, then known as École Supérieure de Pharmacie on rue de l'Arbalète, (N 48° 50.39, E 02° 20.84), 880 meters southeast of the present Faculté de Pharmacie at 4, rue de l'Observatoire. The original plaque at rue l'Arbalète is displayed in the front hallwall of the present Faculté de Pharmacie and dates the school from 1577. The building at rue l'Arbalète now houses an agronomy school (Institut National Agronomique; main entrance at 16, rue Claude Bernard).

3. Henri Jules Debray (1827–1888) appears in the painting portraying the preparation of aluminum by Henri-Étienne Sainte-Claire Deville (1818–1881) in the Sorbonne.[16]

4. There are scores of paintings, reliefs, busts, and statues of Lavoisier,[17] but this statue is, in the opinion of the authors, the grandest. Before WWII a grandiose statue of Lavoisier was positioned in front of Madeleine in Paris, but it was destroyed by the Nazis.[18]

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